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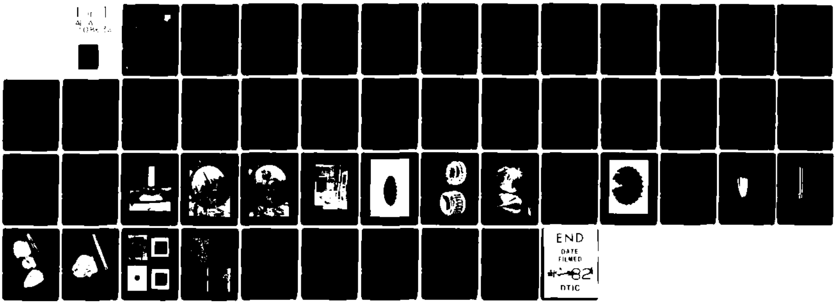

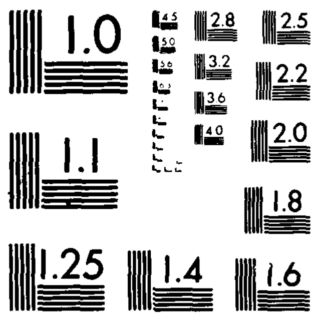

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RADC-TR-81-280
Interim Report
October 1981

GROWTH OF HIGH PURITY OXYGEN-FREE SILICON BY COLD CRUCIBLE TECHNIQUES

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The goal of the program is to explore the feasibility of utilizing a cold crucible system for the growth of high purity, oxygen-free single crystals of silicon. The work includes a detailed evaluation of previous research on cold crucible technology, the design and construction of a cold crucible assembly and the investigation of the growth of single crystals of high purity silicon ~~utilizing~~ the water-cooled cold crucible. In parallel with the experimental work, a theoretical analysis is being carried out on

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the thermodynamics and heat flow characteristics within the melt confined in the cold crucible in an effort to develop a better understanding of the crystal growth process.

The results to date have been ~~most~~ encouraging.

- A water-cooled copper cold crucible (73 mm I.D.) which incorporates a bottom-feeding mechanism, has been designed, constructed and tested.
- Silicon melts (weighing 750 grams) can be routinely melted using low frequency induction heating (250-300 Khz) and confined within the cold crucible for extended periods without contamination.
- Seeding techniques have been developed to permit the Cz growth of single crystals of silicon with lengths up to 100 mm and diameters in excess of 25 mm.
- The preliminary characterization data on the single crystals produced are inconclusive. However, it appears that the purity levels (including oxygen content) of single crystals produced to date are equal to or in most cases, better than, the purity level of the polycrystalline feed material. Typical dislocation densities of the as-grown crystals have been found to be in the range of $4\text{-}5 \times 10^4$ per square centimeter or less. Various crystal growth techniques are now being investigated in an effort to reduce the dislocation level.

TECHNICAL SUMMARY

The two basic methods used to manufacture all of the single crystals silicon used today in the semiconductor industry are the Czochralski (Cz) method and the Floating Zone (FZ) technique. The Cz method i.e crystal pulling from melts contained in quartz crucibles, is the most widely used process at the present time; over 1,000,000 kg of single crystal silicon are produced annually using this process. While Cz-grown crystals exhibit a high degree of crystallographic perfection i.e. dislocation-free crystals are now manufactured on a routine basis, crystal purity, notably oxygen contamination caused by the quartz crucible, is a major problem which impacts upon device performance and yield.

The Floating-Zone (FZ) method, which utilizes high frequency induction heating techniques to produce and maintain a molten zone of silicon without a container, is the only other process used today for large scale silicon crystal production; approximately 200,000 kg of FZ silicon are produced annually. While the purity of FZ silicon crystals is significantly better than Cz silicon crystals (the oxygen impurity level is approximately 100 times less), the typical crystal perfection achieved is limited to a great extent by the thermal geometry inherent to the FZ process. Moreover, the FZ crystals diameter which can be produced is constrained by the volume of molten silicon which can be supported by surface tension combined with RF levitation effects.

Over the past two (2) decades a continuing search has been underway to develop improved, low-cost methods for the production of high purity silicon crystals; ideally, a process which would combine the crystal perfection of CZ crystal production with the purity levels achieved by the containerless FZ techniques. The cold crucible/skull melting technique in which a molten column of silicon is inductively melted and confined within a water-cooled cold crucible structure appears to be a practical combination of the best features of the Cz and FZ methods. Crucible contamination is eliminated by the RF field without physically contacting the walls of the cold crucible. The base of the molten silicon

column is supported on the unmelted portion of the silicon feed material so that the melt is not in contact with any contaminating solid. Moreover, the volume of the melt which can be stably maintained within the cold crucible is not limited by surface tension effects as in the FZ process for example.

The goal of the present program is to explore the feasibility of utilizing a cold crucible system for the growth of high purity, oxygen-free single crystals of silicon. The work includes a detailed evaluation of previous research on cold crucible assembly and the investigation of the growth of single crystals of high purity silicon utilizing the water-cooled cold crucible. In parallel with the experimental work, a theoretical analysis is being carried out on the thermodynamics and heat flow characteristics within the melt confined in the cold crucible in an effort to develop a better understanding of the crystal growth process.

The results to date have been most encouraging:

- A water cooled copper cold crucible (73 mm I.D.) which incorporates a bottom-feeding mechanism, has been designed, constructed and tested.

- Silicon melts (weighing 750 grams) can be routinely melted using low frequency induction heating (~ 250-300 KHz) and confined within the cold crucible for extended periods without contamination.

- Seeding techniques have been developed to permit the Cz growth of single crystals of silicon with lengths up to 100 mm and diameters in excess of 25 mm.

- The preliminary characterization data on the single crystals produced are inconclusive. However, it appears that the purity levels (including oxygen content) of the single crystals produced to date are equal to or in most cases better than, the purity level of the polycrystalline feed material. Typical dislocation densities of the as-grown crystals have been found to be in the range of 4-5 x 10^4 per square centimeter or less. Various crystal growth techniques are now being investigated in an effort to reduce the dislocation level.

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1.0 INTRODUCTION

Silicon is the major semiconductor material used today for device manufacture in the solid state electronics industry. Production of silicon has reached substantial proportions--world-wide output of polycrystalline silicon (the raw material used for subsequent crystal growing operations) exceeded 1,800,000 kg in 1980 and is expected to increase to over 2,400,000 kg in 1981 to meet anticipated production needs (Arthur D. Little, Inc. estimates).

Over the past twenty years, silicon crystal production methods have been steadily developed to provide improved yields, higher purity and lower costs. However, there is growing evidence that further refinement of existing technology or the continued expansion of production capacity utilizing existing production methods, has begun to show diminishing returns in response to the increasingly stringent demands for crystal purity and perfection.

While the production of polycrystalline silicon has become a highly-sophisticated, automated chemical process industry producing tonnage quantities of product with impurity levels in the parts-per-billion range, the production methods used to manufacture single crystal silicon have not kept pace. Indeed, the principal crystal production methods (Czochralski and Floating-Zone techniques) remain batch operations using essentially the same technology developed over 25 years ago - although greatly expanded to meet the increasing capacity needs of the semiconductor industry.

The two basic methods used to manufacture all of the single crystal silicon used today in the semiconductor industry are the Czochralski (Cz) method and the Floating-Zone (FZ) technique. The Cz method, which is the most widely used process at the present time, involves the growth of a silicon crystal (via vertical-pulling) from molten silicon which is contained in a fuzed quartz crucible. Over 1,000,000 kg of single crystal (up to 125 mm diam.) are grown annually via this process utilizing sophisticated Cz furnace systems which contain silicon melts weighing up to 40 kg. Automatic crystal diameter/melt temperature controls are used to produce high yields of silicon crystal which are virtually dislocation-free. Unfortunately, silicon melts

react with the quartz container and Cz-grown silicon crystals are found to contain a significant quantity of impurities such as oxygen which necessitates further processing to reduce its electrical activity.

The Floating-Zone (FZ) method is the only other process used today for large-scale silicon crystal production; approximately 100,000 to 200,000 kg of FZ crystal with diameters up to 100 mm are produced annually. In the FZ process, high frequency induction heating is used to melt a portion of a polycrystalline silicon feed rod. The molten zone, which is axially-supported by the surface tension of the melt, is seeded (as in the Cz method) and by moving the molten zone away from the seed/melt interface, controlled nucleation and crystal growth is allowed to take place.

While the FZ process permits the production of silicon crystals which contain less oxygen impurity (about 100 times less), striations are more pronounced in FZ crystals because the thermal conditions in FZ furnaces are less symmetrical than those typically found in Cz pullers.

Over the past two decades, a continuing search has been underway to develop improved, low-cost methods for the prodution of high purity silicon crystals. Containerless methods, similar to the FZ process, have been pursued as a means of improving crystal purity. Levitation methods have also been explored in which the silicon is not only melted by RF induction heating, but also physically supported by the RF field. While this melting technique has proven to be an intriguing concept, the weight of the silicon melt which can be fully levitated by the RF field is severely limited, thus restricting the process to research applications.

Cold hearth melting and casting of refractory metals using induction heating methods were described in the early 1960's. However, in 1966, researchers at TOCCO-STEL (France), a manufacturer of induction heating equipment, were the first to successfully adapt a skull-melting/cold-crucible approach to the fusion of silicon. Using this technique, the molten column of silicon which is confined in a water-cooled cold-crucible structure is squeezed radially and contained by the RF field. The base of the molten column is supported on the unmelted portion of the feed material; indeed, the melt is physically

supported but is not in contact with any contaminating solid.

A French patent was granted on this process (U.S. Patent applications were never filed) and other than the patent document, details of this work were never published, nor to our knowledge pursued further.

In 1977, with internal funding, researchers at Ceres Corporation initiated an intensive program on the adaption of cold-crucible technology to the fusion and recrystallization of high purity silicon. Using a cold-crucible assembly of proprietary design, Ceres' researchers succeeded in pulling poly-crystalline silicon ingots from melts confined in the cold-crucible. Results of Ceres' preliminary experiments demonstrated that this new technique could be used to maintain large, stable melts of silicon with minimal, if any, oxygen contamination.

During the course of the present program, techniques have been established for the growth of single crystals of silicon from melts confined in a cold-crucible and preliminary characterization data indicates that the purity level of the silicon single crystals have been significantly enhanced during the growth process.

2.0 TECHNICAL DISCUSSION

2.1 BACKGROUND INFORMATION

2.1.1 THE NATURE OF OXYGEN IN SILICON CYRSTALS

Currently in the semiconductor industry more than 75% of the silicon crystals are grown by the Czochralski (Cz) method. In this method, quartz (SiO_2) crucibles and graphite heaters are used. The surface of the crucibles which are in contact with the silicon melt is gradually dissolved into the melt by the reaction $SiO_2+Si \longrightarrow SiO$. This reaction during crystal growth contributes to the presence of oxygen in silicon crystals.

When a silicon crystal is pulled, oxygen is incorporated into the silicon lattice as a solid solution, with the maximum solubility of oxygen in silicon at its melting point being approximately 2.0×10^{18} atmos/cc. Oxygen occupies the interstitial sites of silicon lattice and gives the bonding configuration of Si-O-Si. However, during heat treatment, oxygen may rearrange within the silicon lattice to form other types of bonding(1,2). Change in the oxygen bonding leads to changes in the electrical and structural properties of silicon(3).

The concentration of oxygen in the silicon crystal is affected by crystal growth parameters. It has been observed that the concentration increases with the rotation of the crystal or crucible(4). Karimov and Sunyukov(5) have found that a pull rate of 1.5 to 2.0 mm/min gives the highest oxygen concentration; increasing or decreasing the pull rate from this range leads to a decrease in oxygen content.

Another parameter which effects the oxygen concentration is the pressure of the growth environment. A reduction in furnace pressure tends to decrease the oxygen content in the grown crystal.

The concentration of oxygen in silicon crystals is also affected by the diameter

ratio of crystal to crucible. This is manifested by the variation of oxygen concentration along the axial direction of the tapered section of the crystal. There is strong evidence to suggest that oxygen concentration increases with the ratio of crystal to crucible diameter.

The concentration of solid soluble oxygen in silicon can be affected by thermal annealing. This effect becomes obvious when the as-grown crystals are supersaturated with oxygen and the crystals are heat-treated for a prolonged period of time.

There are several harmful affects of the presence of oxygen in silicon crystals. Generation of oxygen donors by heat treatment at 450°C for example confuses the measurement of dopant concentration via resistivity readings. The presence of oxygen donors will also affect the predicted voltage breakdown and other electrical parameters of a P-N junction device. A second phase precipitate (SiO_2) observed in the heat-treated wafers (700-1000°C) is due to oxygen in the silicon crystals[3,6].

Other types of process-induced defects such as swirls and oxidation-induced stacking faults have been correlated to the presence of excess oxygen concentration (< 25 ppm)[7,8].

In an effort to minimize and hopefully eliminate the problems of oxygen impurity in silicon, various crucible-free methods of crystal growth have been explored with limited success. The Floating Zone method comes closer to eliminating oxygen contamination; however FZ·grown crystals still contain oxygen (typically about 1/100 that of CZ-grown crystals) which is introduced in the feed material, and the problem of oxygen contamination persists.

2.1.2 APPLICATION OF COLD CRUCIBLE/SKULL-MELTING TECHNOLOGY TO THE GROWTH OF SILICON CRYSTALS

The earliest work on cold-crucible ("skull") melting was described in a German Patent filed by Siemens and Halske in 1926[9] and it appears that

the technique was not further developed at that time. In 1960, Sterling and Warren[10] reported on their extensive investigations of contamination-free, high temperature melting in several versions of the cold-crucible. They showed that by modificaton of the shape of a water-cooled hearth the interaction between inducing and induced currents could produce varying degrees of electromagnetic levitation of the melt from the surface of the hearth. The use of cold-boats and crucibles constructed on this principle for zone refining and consolidation have been very successful and they have been well summarized by Bunshah[11]. Cage crucibles such as that described by Sterling[10], Rummel[12] and Hukin[13] have been used successfully for the growth of silicon crystals via the Czochralski technique. It is worth noting however, that these particular cold-crucible configurations are designed to fully-levitate the melt and are, therefore, quite limited in the weight or volume of liquid which can be supported by the RF field.

In 1966, Blieck and Reboux[14] first reported upon a "skull" approach to the melting of silicon. In this case, the silicon melt is confined in a water-cooled, cold-crucible structure and the molten column is radially-squeezed by the RF-field and does not contact the walls of the container. The base of the liquid silicon column is supported on the unmelted silicon feed rod so that the melt is not contaminated by contact with any foreign material. Stable silicon melts were achieved, but subsequent crystal growing experiments were not carried out[15]. Other than the patent document, details of this work were not published.

In 1977, Ceres Corporation initiated an intensive program (internally funded) to investigate the adaptation of cold-crucible technology to the fusion and recrystallization of high-purity silicon. Utilizing a cold-crucible assembly of proprietary design, Ceres researchers succeeded in producing and maintaining relatively large (~ 400 gms) stable melts of silicon via direct RF induction heating at low frequencies (250-300 KHz).

Large-grain, polycrystalline silicon ingots pulled from melts confined in the cold-crucible were analyzed; the resultant purity levels were found to be at

least equal to, or in most instances, better than the semiconductor-grade polysilicon feed stock employed. Based upon the demonstrated potential of the basic cold-crucible/silicon process, Ceres embarked upon the present program in an effort to establish the feasibility of producing oxygen-free single crystals of silicon.

2.2 GOALS OF THE PROGRAM

The goal of the program is to explore the feasibility of utilizing a cold-crucible system for the growth of high purity, oxygen-free single crystals of silicon. The work includes the following tasks:

I - Investigation of previous research on cold crucible technology and in particular, as it relates to the growth of high-purity silicon crystals.

II - Study the design and construction of presently available cold-crucible assemblies to determine if modifications and/or redesign is necessary to achieve the overall goals of the program.

III - Design and/or modify selected cold-crucible configuration(s) to permit continuous or quasi-continuous feeding operation.

IV - Testing and evaluation of the cold crucible assembly for the growth of high purity, oxygen-free silicon crystals.

V - Investigate and perform theoretical studies as deemed necessary, of the thermodynamics and heat flow patterns as related to:

a.) The placement of the cylindrical silicon charge in the cold crucible.

b.) The necessity, configuration and location of a surface thermal reflector.

c.) The requirement, design and configuration of seed crystal heating.

VI - Delivery of the cold crucible assembly(ies) and silicon crystal specimens.

2.3 PROGRESS TO DATE

2.3.1 LITERATURE/PATENT SEARCH

An extensive literature/patent search on RF induction melting and cold crucible technology, particularly as it relates to the production of high purity silicon crystals, has been carried out. To date, several hundred relevant journal articles and patents have been obtained (and translated as necessary) and are in the process of being indexed and catalogued.

Selected references, particularly those relating to the induction heating of silicon, are being reviewed and correlated with the results of silicon fusion experiments carried out to date in the cold crucible.

2.3.2 DESIGN AND CONSTRUCTION OF THE COLD CRUCIBLE ASSEMBLY

The basic design criteria for the cold crucible assembly was developed during the course of an earlier program supported by the Air Force Cambridge Research Laboratories[16]; the theoretical analysis of this system was further developed by Scott and his co-workers at Los Alamos Scientific Laboratory[17].

The cold crucible assembly which has been developed during the course of this program is illustrated in Figure 1. It combines the features of the earlier AFCRL system[18] with a bottom-feeding arrangement developed prior to the start of this program by Ceres Corporation for the production of cubic zirconia crystals via the skull melting process.

Basically the cold crucible assembly is a cylindrical structure having an internal diameter of 73 mm and an overall height of approximately 350 mm. Twenty-six 1/4" diam. (6.35 mm) copper tubes (each with a separation of approximately 1/2 mm) form the cylinder. Each closed-end tube is provided with a concentric cooling water outlet; i.e. the cooling water is forced upwards between the walls of the inner and outer tubes and drained via the inner tube. Each of the outer tubes is brazed to a copper, o-ring sealed flange which can be removed to facilitate tube repairs and/or replacement.

The water-cooled base plate of the cold crucible is electrically isolated by a teflon flange from the tubular wall of the structure. The base may be raised or lowered (while the cold crucible is in operation) over a total stroke of 200 mm. Adjustment of base height can be used to vary the height of the silicon melt within the RF coil or alternatively, to introduce polycrystalline silicon feed stock during the crystal growing operation.

The cold crucible assembly is fastened to the furnace base by the cooling water inlet/outlet tubes which are threaded to accept brass clamping nuts. It is worth noting that the entire cold crucible assembly is electrically isolated from the furnace chamber by O-ring sealed teflon glands and flanges. The cold crucible structure mounted on the furnace base plate is shown in Figure 2.

Numerous RF coil configurations are being investigated in an effort to optimize RF coupling to the silicon charge. A closely-coupled, 6 turn coil (6.35 mm copper tubing) with an overall height of 65 mm, operating at 250 KHz is currently used for the silicon melting/crystal growing experiments.

The high resistivity of semiconductor-grade polycrystalline silicon feed material at room temperature, does not permit direct coupling by the RF field and some means of preheating must be incorporated into the cold crucible furnace structure. A graphite disc (6.35 mm thick) which is heated by the RF field, can be positioned above the cold crucible to preheat the silicon charge (as shown in Figure 3). When the silicon charge is radiatively heated to approximately 800°C to permit direct RF coupling, the graphite disc, which is mounted on a water-cooled stainless steel shaft, can be moved aside (as shown in Figure 4) to facilitate the melting and crystal growing operations.

2.3.3 TESTING AND EVALUATION OF THE COLD CRUCIBLE ASSEMBLY

Testing and evaluation of the cold crucible assembly is being carried out in the Czochralski-type crystal growing furnace shown in Figure 5. The water-cooled stainless steel furnace chamber is capable of operating at pressures

ranging from 10^{-3} torr to 1 atmos.

A manually-operated screwlift mechanism has been incorporated below the furnace chamber to raise or lower the water-cooled baseplate of the crucible assembly.

Cold crucible silicon melting experiments which were carried out at Ceres prior to the initiation of the present program indicated that high frequency (3-5 MHz) RF power could not be used to achieve complete melting of the polycrystalline silicon charge confined in the cold crucible. Using a 50 KW output RF power supply operating at approximately 3.5 MHz, a silicon charge (typical weight 450 grams) could not be melted.

Using a 50 KW output, low frequency (250-300 KHz) RF power supply (which incorporates a variable-ratio, low voltage-output transformer to minimize sporadic arcing) we were successful in producing and maintaining stable melts of silicon (approx. wgt. 750 gms.) which are confined by, but not in physical contact with the tubular wall of the cold crucible assembly.

The typical start up and operating procedures used to produce a silicon melt confined in the cold crucible are as follows:

a.) Discs of semiconductor-grade polycrystalline silicon feed rod (Hemlock Semiconductor Inc.) approximately 20 mm thick (nominal diameter 70-72 mm) which have been cleaned and etched after slicing, are stacked on the baseplate of the cold-crucible assembly (total weight approximately 800 gms.).

b.) The graphite disc preheater is positioned over the charge (as shown in Figure 3) and the furnace chamber is sealed and evacuated.

c.) Following several flushing and evacuation cycles, the chamber is filled with argon/5% hydrogen to approximately 1 atmosphere.

d.) The RF power (at 250 KHz) is turned on and coupled to the graphite disc

preheater which is heated rapidly to approximately 1000°C. Within a few minutes, the upper surface of the silicon charge is radiantly heated sufficiently to permit direct RF coupling and the preheater is moved aside as shown in Figure 4.

e.) Silicon melting progresses slowly from the wall of the silicon discs inward. Early stages of melting resemble a mushroom shape i.e. a solid silicon core (or stem) topped with a solid silicon cap surrounded by the melt which is not in contact with the inner surface of the cold crucible.

f.) The thin solid silicon cap is the last remnant of the charge to be melted and a typical melt is shown in Figure 6.

It is worth noting that the silicon melt (approx. 73 mm diam. and 60 to 70 mm deep) is supported on an unmelted disc of the polycrystalline silicon feed rod which is in direct contact with the water-cooled cold crucible base plate. However, the RF field exerts a uniform squeezing force on the side of the cylindrical melt with the result that there is a visible separation (approx. 1/2 mm) between the melt and the water-cooled cold crucible.

The silicon melting experiments were terminated by merely shutting off the RF power. Typical quenched silicon melts are shown in Figure 7. The imprint of the copper tube wall structure on the wall of the ingots is the result of the sudden removal of the RF field and the relaxation and freezing of the melt against the copper tube wall of the cold crucible.

2.3.4 RESULTS OF SILICON CRYSTAL GROWING EXPERIMENTS

Initial attempts to pull single crystals of silicon by the Czochralski technique from melts confined in the cold crucible resulted in the growth of large grain polycrystalline ingots as shown in Figure 8. Wetting of the silicon seed crystal by the melt proved to be extremely difficult to achieve. When the etched seed (5 x 5 x 50 mm/111-orientation) was immersed into the melt and held for 30 minutes prior to withdrawal, there was no evidence of seed wetting or melting.

Attempts to raise the melt temperature by increasing the applied RF power proved to be fruitless i.e. at the maximum RF power level (50 KW) it was not possible to initiate seed wetting. The furnace system incorporating the cold crucible was then transferred to a 120 KW output, direct tank-loaded, RF power supply (operating at 250-300 KHz) and a series of experiments was initiated in an effort to increase the silicon melt temperature. Despite the application of higher RF power levels (up to 100 KW), the silicon melt temperature was not increased sufficiently to promote seed wetting. However, we did cause intermittent boiling of the cooling water flowing through the cold crucible.

We were forced to conclude that it was not possible to raise the temperature of molten silicon significantly by direct induction heating techniques. Our experimental results were confirmed upon examination of the electrical conductivity data for solid/molten silicon[19] i.e. solid silicon @ 1420°C has an electrical conductivity of 316 mho/cm which increases dramtically to 10^4 mho/cm for molten silicon at the same temperature. The very high electrical conductivity of molten silicon effectively limits the low frequency RF power input to the melt.

In light of the practical difficulties encountered in raising the silicon melt temperature, we decided to explore the alternative of independently controlled heating of the seed to promote seed-wetting.

A resistance-heated silicon seed holder as shown schematically in Figure 9, was designed and constructed. A miniature nichrome resistance heating element was contained within a transparent quartz tube enclosing the upper end of the silicon seed. Power leads for the resistance-heating element were incorporated in a hollow, stainless steel seed shaft. Ceramic-to-metal gas-tight seals were used to terminate the power leads within the chamber. Since the seed shaft must be raised or lowered and rotated simultaneously, a slip-ring assembly is attached to the exposed end of the seed shaft to transmit power from a Variac control to the heating element.

A series of silicon crystals growing experiments were carried out using the

resistance-heated seed holder (see Figure 10). At heater temperatures of 800-900^{o}C, wetting of the seed by the silicon melt was improved marginally but it was apparent that a higher-temperature heat source was necessary to insure reproducible seeding of the silicon melt.

The mechanical and electrical requirments of a larger (higher temperature) resistance-heated seed holder imposed significant practical limitations not only on the furnace system but on the crystal pulling operation itself, and a decision was made to explore alternative methods of seed heating.

A conical graphite reflector was designed and constructed as shown in Figure 11. Fabricated from high purity (AVC Grade) graphite, the truncated cone incorporates two (2) small viewing ports and rests on three (3) quartz rod supports, above but not in electrical contact with, the cold crucible assembly. The cone is heated directly by the RF field. Initial tests indicated the need to incorporate a graphite wool or foam insulation on the outer surface to reduce the radiant-heat loss. The use of the graphite reflector/radiator eliminated the need for the graphite disc preheater as shown in Figure 3.

Utilizing the graphite reflector/radiator, we succeeded in raising and maintaining the silicon seed temperature sufficiently to promote wetting of the seed by the melt and the controlled growth of single crystals of silicon. Two single crystals of silicon grown with the reflector/radiator in place are shown in Figures 12 and 13. They were pulled at a rate of 2.5 cm/hr with a seed rotation rate of 6 RPM. It is worth noting that the resultant crystals diameters were manually controlled. The maximum crystal diameter is physically limited by inner diameter (~ 40 mm) of the top of the graphite cone.

When withdrawn rapidly from the melt the crystal/melt interfaces appear to be flat and planar (Figure 14). We have also noted that as the melt level is lowered during the crystal pulling operation, the core of the growing crystal remains molten while the outer surface continues to solidify as a single crystal; this effect is shown in Figure 15. When the growing crystal is rapidly withdrawn from the melt, the molten core spills out leaving a cavity approximately 2 cm deep.

The solid (single crystal)/melt interface is planar and the single crystal wall is approximately 2 mm thick. It appears that as the melt is lowered within the RF coil during the crystal growing operation, the RF field (@ 250 KHz) remains coupled to the molten core of the crystal while the surface is cooled by radiation and solidifies. It is anticipated that the molten core phenomenon can be controlled by maintaining a constant melt level throughout the crystal growing operation by actuating the baseplate lift mechanism (i.e. bottom-feeding).

2.3.5 CHARACTERIZATION OF SILICON MATERIAL

Representative samples of the polycrystalline silicon feed material (Hemlock Semiconductor Corp.) and single crystals of silicon grown from melts confined in the cold crucible have been submitted to the Technical Contract Manager (RADC/ESM) for characterization and analysis.

The samples were, in turn, provided to an RADC vendor (Manlabs, Inc.) and the Air Force Wright Aeronautical Laboratories (AFWAL/MLPO) for analysis. Preliminary results are presented below:

MANLABS RESULTS

Dislocation Densities

A single crystal of silicon (111) orientation, was sectioned and then etched in order to obtain a measure of the dislocation densities in the crystal. The etch pit count of surfaces that have been etched using the Dash etch (5:3:3::: HNO_3:HF:CH_3:COOH) followed by a Sirtl decoration etch provide densities in the range of 10^4 to 10^5 dislocations per cubic cm. Details showing the typical dislocation distributions are presented in Figures 16 and 17.

Chemical Analysis - Trace Elements

Samples in the form of long, needle-like rods were cut from both the starting

polycrystalline material and from the single crystal grown from that starting material. The samples were then used as the electrodes in a mass spectrographic instrument and an analysis made of all possible elements in the two types of silicon.

In order to eliminate any surface contaminants, the "electrodes" were etched in Ultex HNO_3.HF. Dist. H_2O reagents and rinsed in deionized water and dried with acetone. The sample electrodes were than pre-sparked for about 15 minutes before experimental spectra were recorded. The normal procedure is to record several spectra at different exposure conditions during the sparking of the electrodes such that experimental variables can be calibrated during the analysis. It was found that during such sequential recording during the sparking of these samples, the electrodes showed considerable inhomogeneity along the length of the electrode. The inhomogeneity noted for several types of elements are indicated in the data.

MASS SPECTROGRAPHIC ANALYSIS

(Concentrations in parts per million by weight)

Element	Silicon L**(Poly Crystal)	Silicon S (Single Crystal)
B	0.03	0.01
Na	-	*1
Mg	-	*1
Al	2	*0.3
P	0.5	0.3
Cl	0.5	0.5
K	4	1
Ca	0.7	1
Cr	*0.4	*10
Mn	0.02	0.02
Fe	1	0.6
Ni	0.4	0.4
Cu	*0.4	*1

*These elements were inhomogeneously distributed along the length of the sample electrode. It was also noted that carbon was detected but the data are qualitative and did show similar inhomogeneities.

**Hemlock Semiconductor Corp., poly-silicon Lot No. SB070189.

Carbon/Oxygen Contamination

The total carbon and total oxygen content in these samples have been determined using a LECO combustion-type apparatus. The data from the measurements are:

	% Carbon	%Oxygen
Sample L (Polycrystalline)	0.0064 0.0073 0.0079 (0.0072)	0.0021 0.0023 (0.0022)
Sample S (Single Crystal)	0.0153 0.0126 0.0143 (0.0140)	0.0010 0.0025 0.0019 (0.0018)

Triplicate determinations are made when the difference between the first two data points show significant spread in their values. In terms of other units, note that 0.0072%, for example, is the same as 72 ppm.

These data suggest that during the growth process, the silicon seems to have picked up some carbon, with the value increasing from 72 ppm to 140 ppm. There does not seem to be any significant difference in the oxygen levels in the two types of materials. Both materials have oxygen concentrations in the 18 to 22 ppm range.

The determination of the oxygen and carbon in samples of this same material have also been made using a fast Fourier transform infrared transmission method on 2 mm thick sections of unpolished material. The data is as follows:

	Carbon	Oxygen
Sample L (Polycrystalline)	1.2 ppm	4.9 ppm
Sample S (Single Crystal)	2.6 ppm	5.8 ppm

The data obtained form the IR transmission measurements are based on a series of calculations defined by the position of the transmission maximum in the spectra. Hence, the position of that peak can significantly influence the background corrections, the shape and sharpness of the peak and several other experimental factors. The data presented here were obtained from only one measurement on one sample that may not have been optimized in the surface preparation. The

data are very semi-quantitative but can be used to compare the two materials.

The FFT data suggest that the single crystal material does contain more carbon than the starting material. The ratio of the carbon concentrations are about the same for the FFT data and LECO combustion data.

The spectra obtained from these silicon samples did show a relatively strong transmission band near the spectra range of about 1200 wave numbers. The bands in that region are normally associated with silicon oxygen bands found in many of the silicon oxide-type compounds. Because of that band, due to a precipitated form of the oxide (silicon oxide or dioxide, for example) it is difficult to estimate the concentration of the interstitial oxygen. The values reported for these samples could be in error due to this interference. The data, however, do suggest that the oxygen concentration in the two samples is about the same.

The exact relationship between the two methods of determining the carbon and oxygen content in silicon is a subject still under discussion. Hence, these data should be considered as preliminary and semi-quantitative until additional measurements can be made on other samples.

AFWAL/MLOP RESULTS

For a single crystal silicon ingot pulled from the cold crucible.

Hall Data

Resistivity = 21.9 ohm-cm.

$N_D = 4.8 \times 10^{18}\ cm^{-3}$ (donor conc.)

$N_B = 7.6 \times 10^{14}\ cm^{-3}$ (boron conc.)

Disclocation Density

$4 \times 10^4\ cm^{-2}$

Spark Source Mass Spectrometry (by Charles Evans & Associates, San Mateo, CA).

Element	Single Crystal Silicon	Polycrystalline Silicon	Range Factor	Range Rank
B	0.02	0.02	1	2
Mg	---	1	0	1
Al	0.05	0.1	2	3
Si	Major	Major	---	---
P	0.05	0.5	10	6
Cl	0.2	0.05	4	4
K	0.5	---	0	1
Ca	0.1	0.5	5	5
Cr	0.02	0.3(inhomogeneous)	15	7
Mn	0.02	---	0	1
Fe	0.3	0.3	1	2
Cu	0.03	0.2(inhomogeneous)	10	6
As	*0.01	---		

*Not confirmed

All concentrations in parts per million

Elements *not* detected less than 0.05 parts per million atomic, unless otherwise noted.

Absolute accuracy x/÷ a factor of 3.

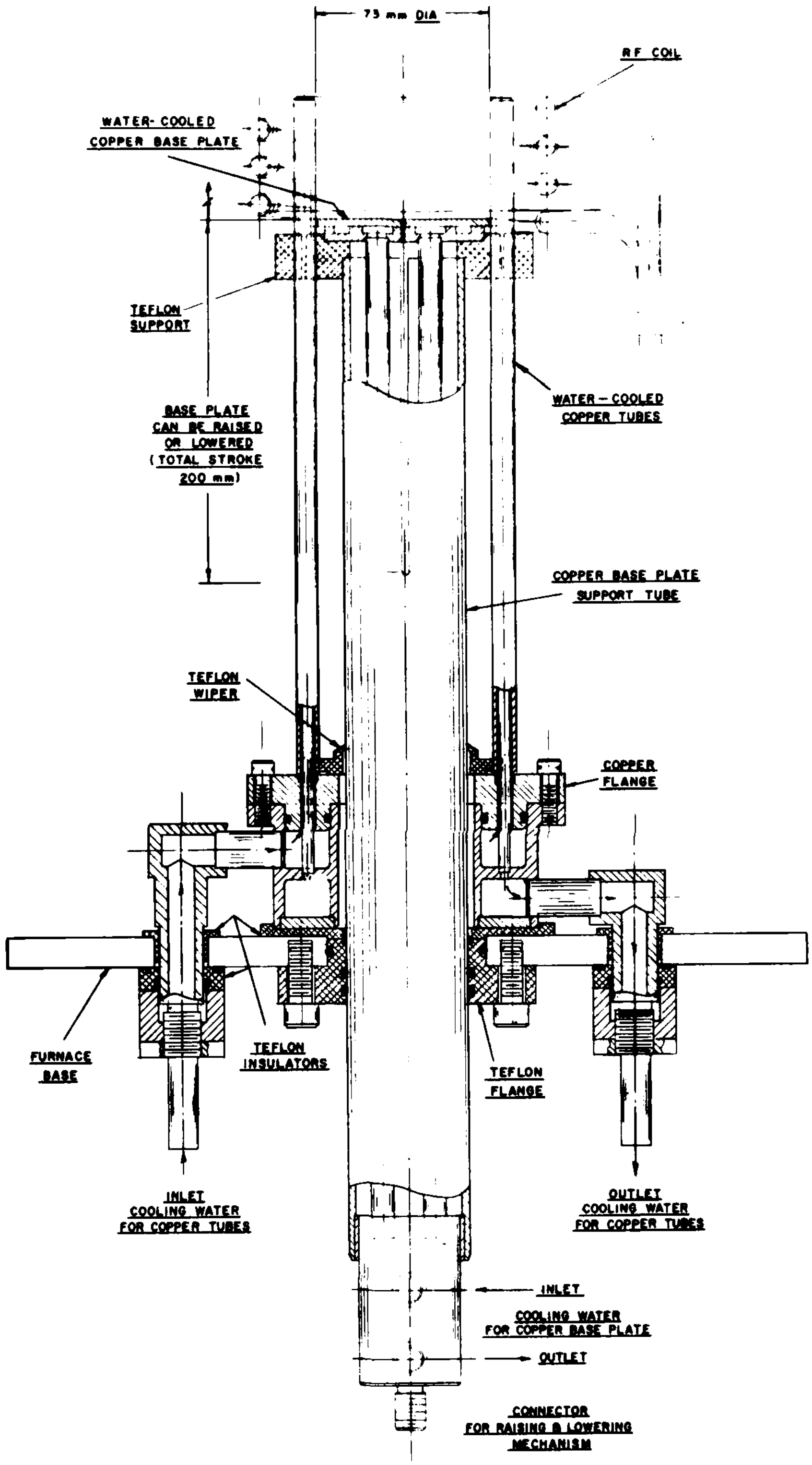


FIGURE 1 WATER COOLED COLD CRUCIBLE ASSEMBLY

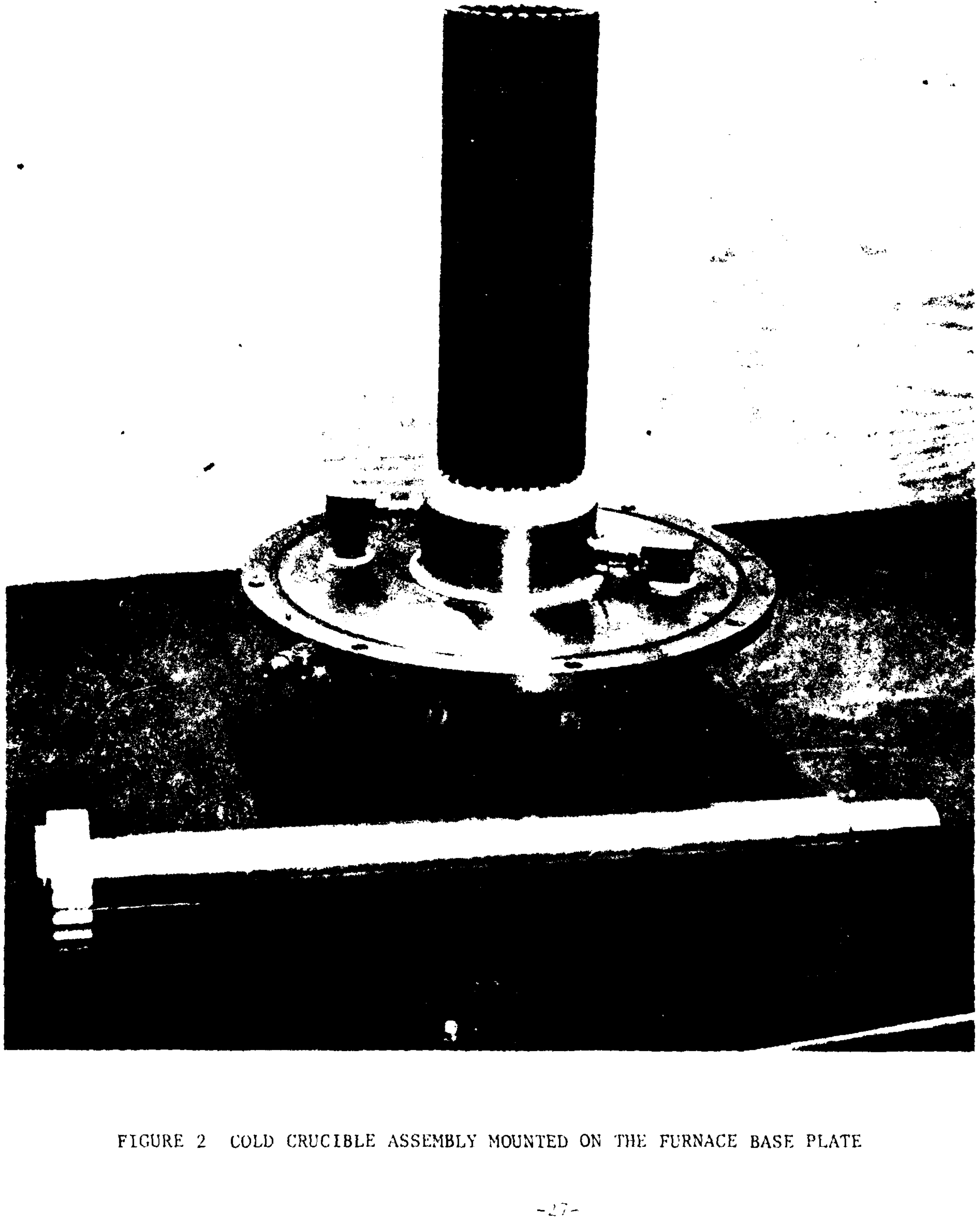
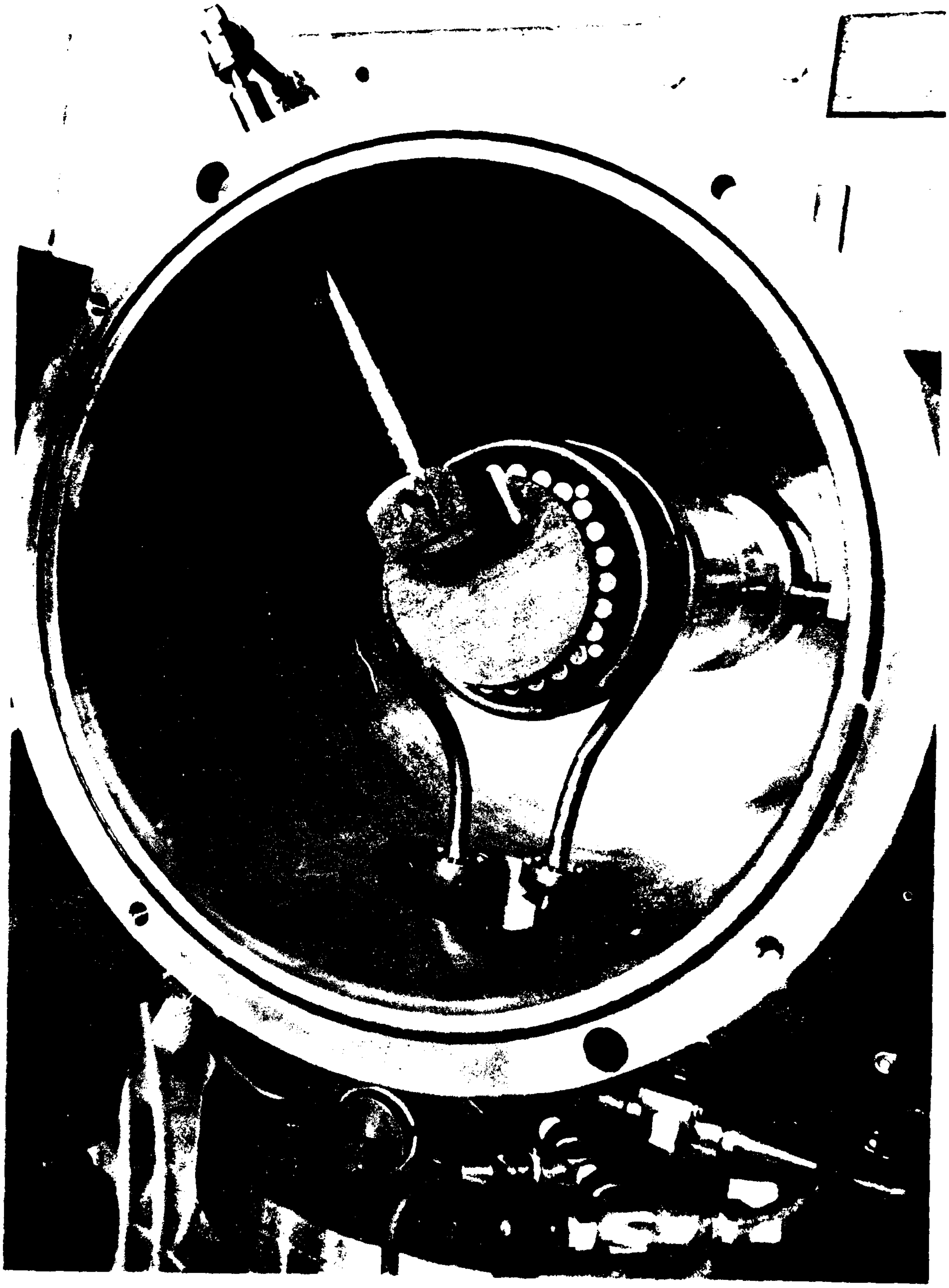
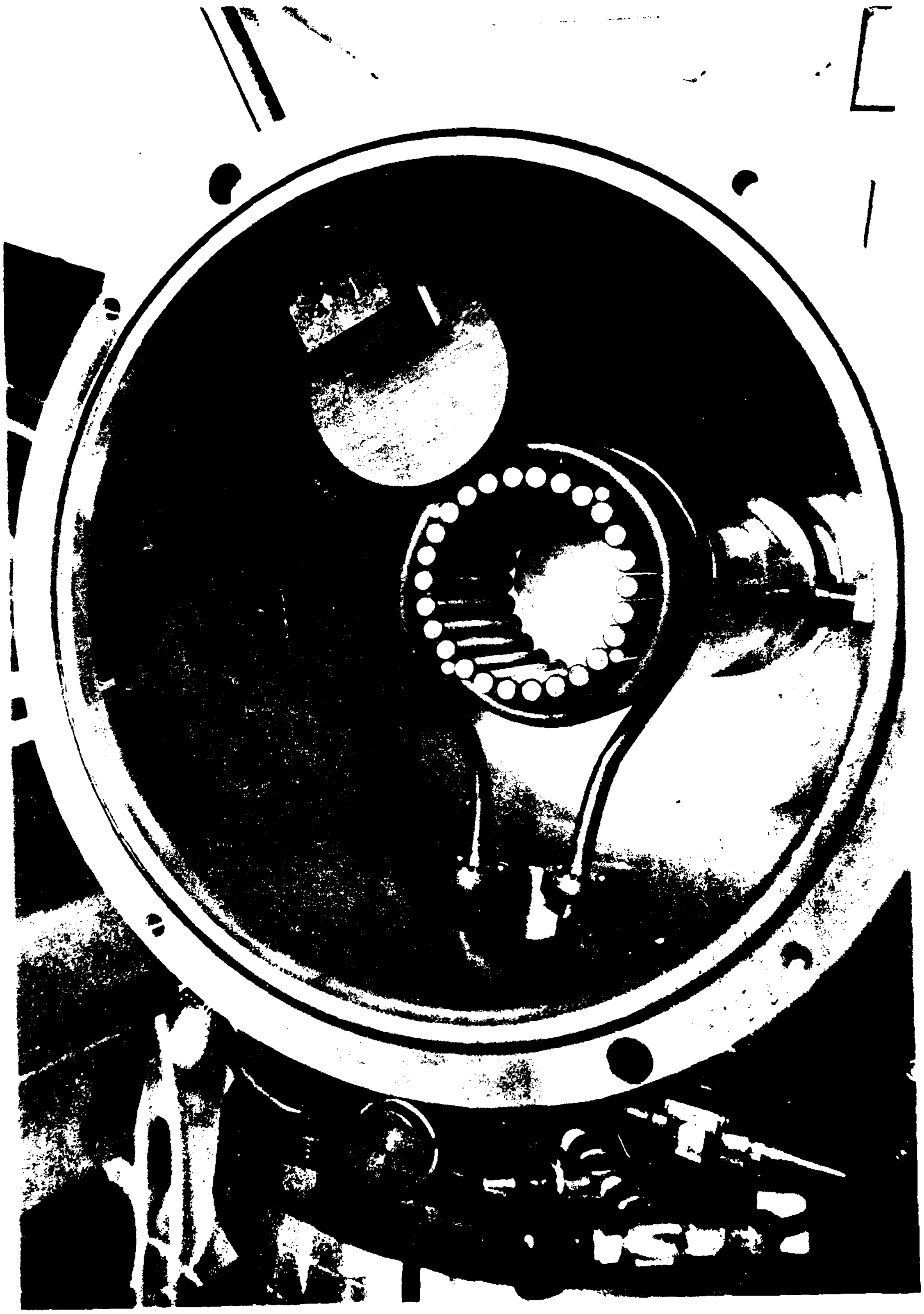


FIGURE 2 COLD CRUCIBLE ASSEMBLY MOUNTED ON THE FURNACE BASE PLATE





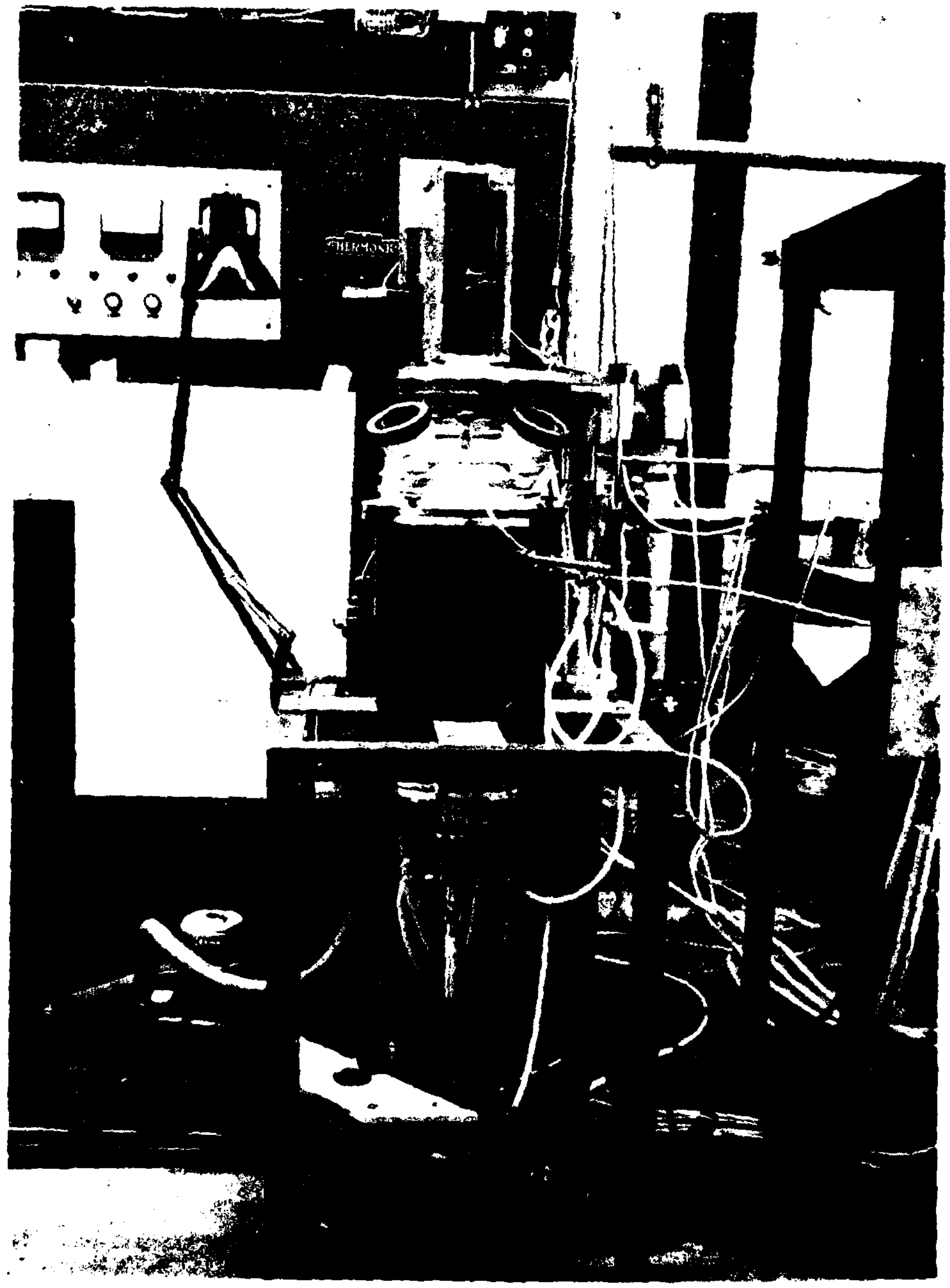
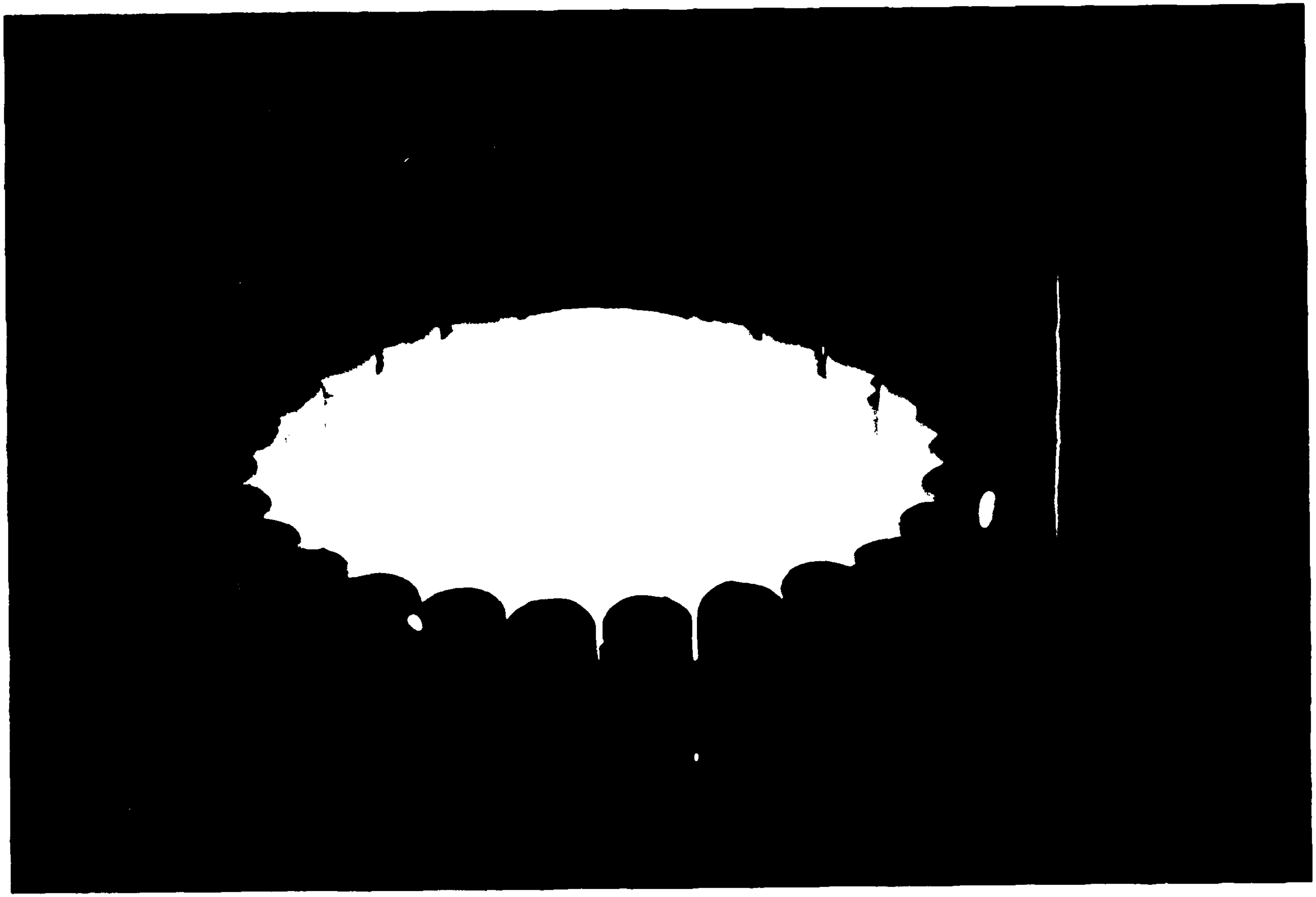


FIGURE 5 CZOCHRALSKI-TYPE CRYSTAL GROWING FURNACE CONTAINING THE COLD CRUCIBLE ASSEMBLY



6. SILICON MELT CONFINED IN THE COLD CRUCIBLE

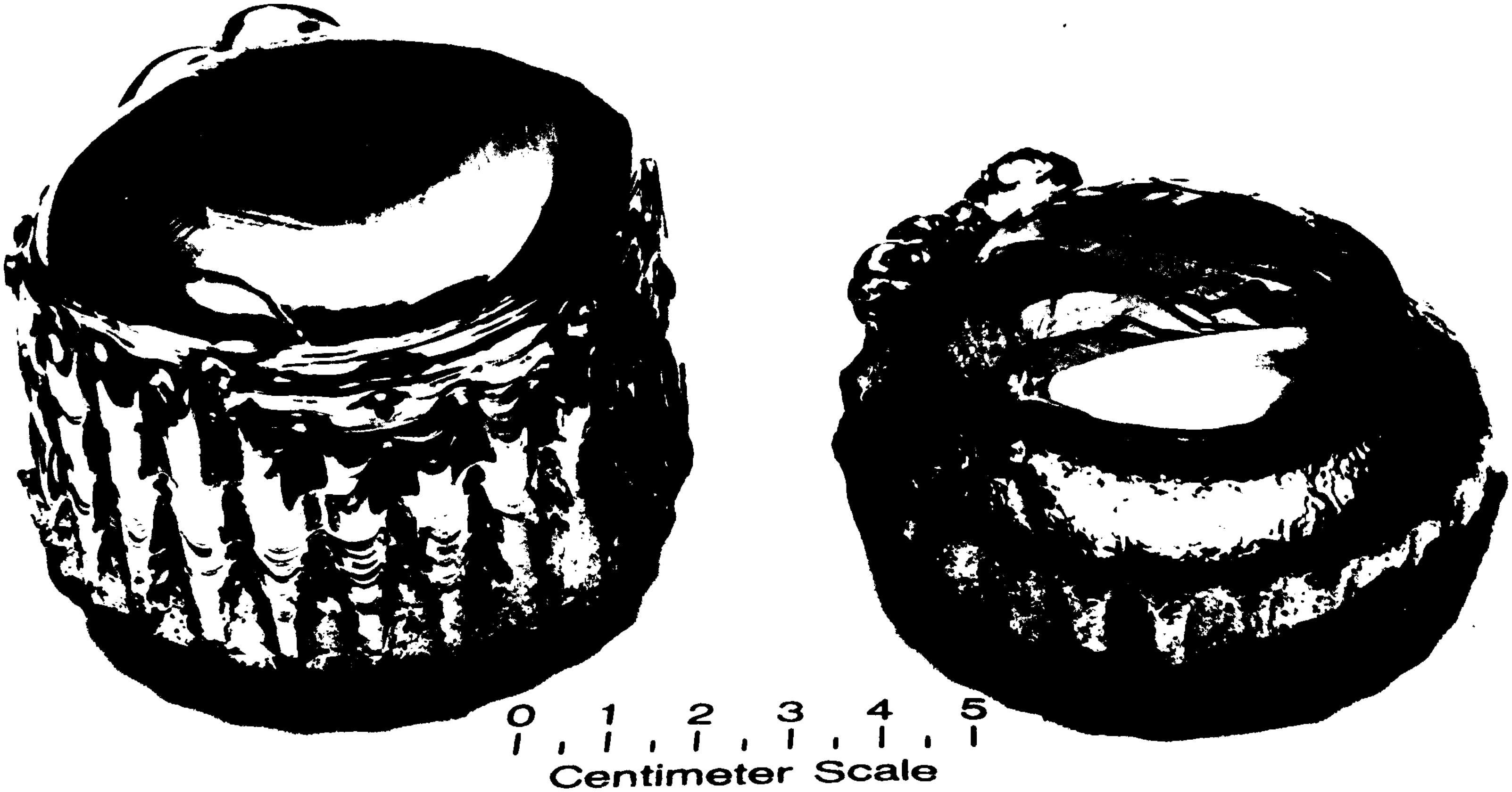


FIGURE 7 QUENCHED SILICON MELTS REMOVED FROM THE COLD CRUCIBLE

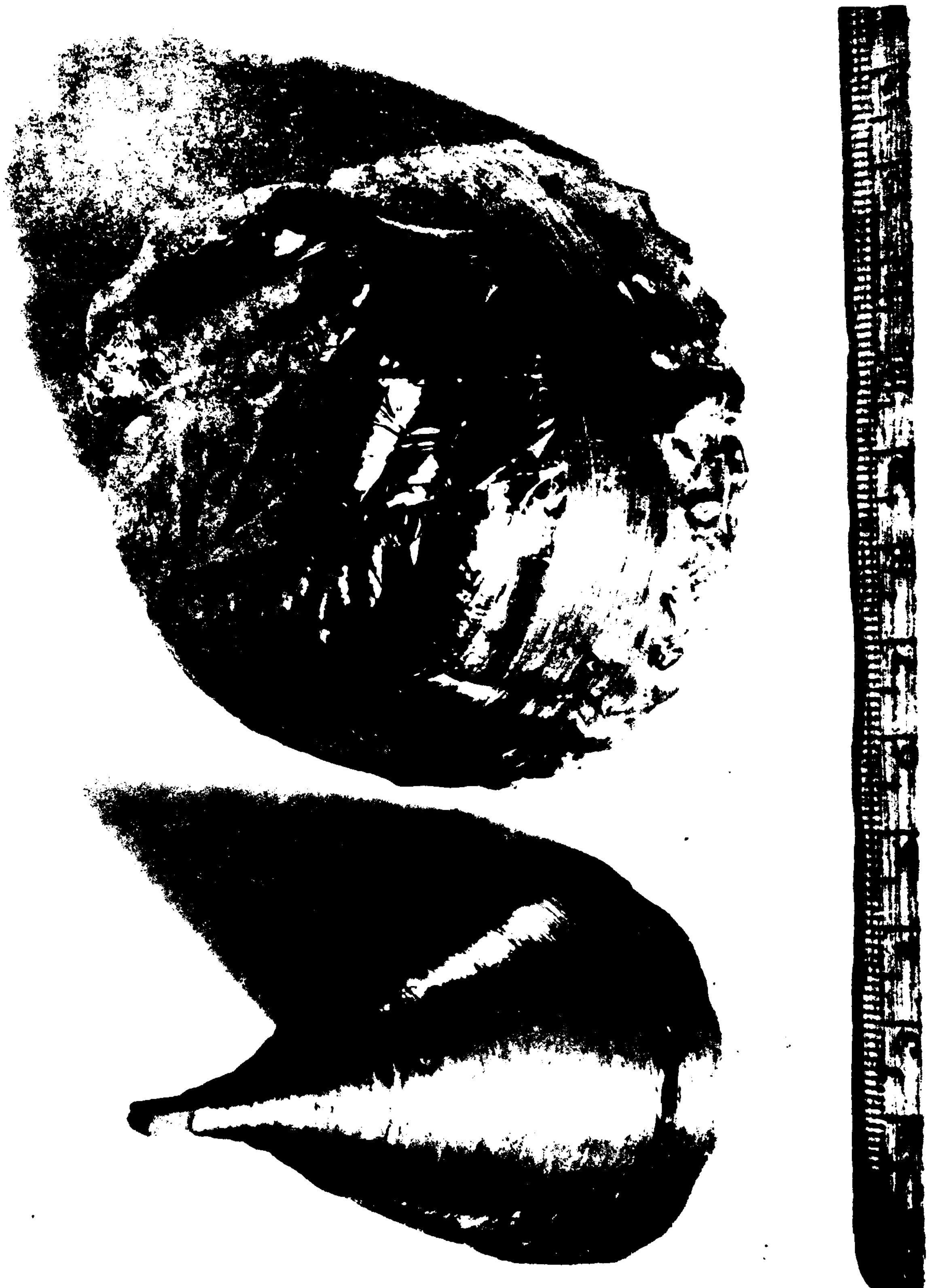


FIGURE 8 POLYCRYSTALLINE SILICON INGOT PULLED FROM THE COLD CRUCIBLE

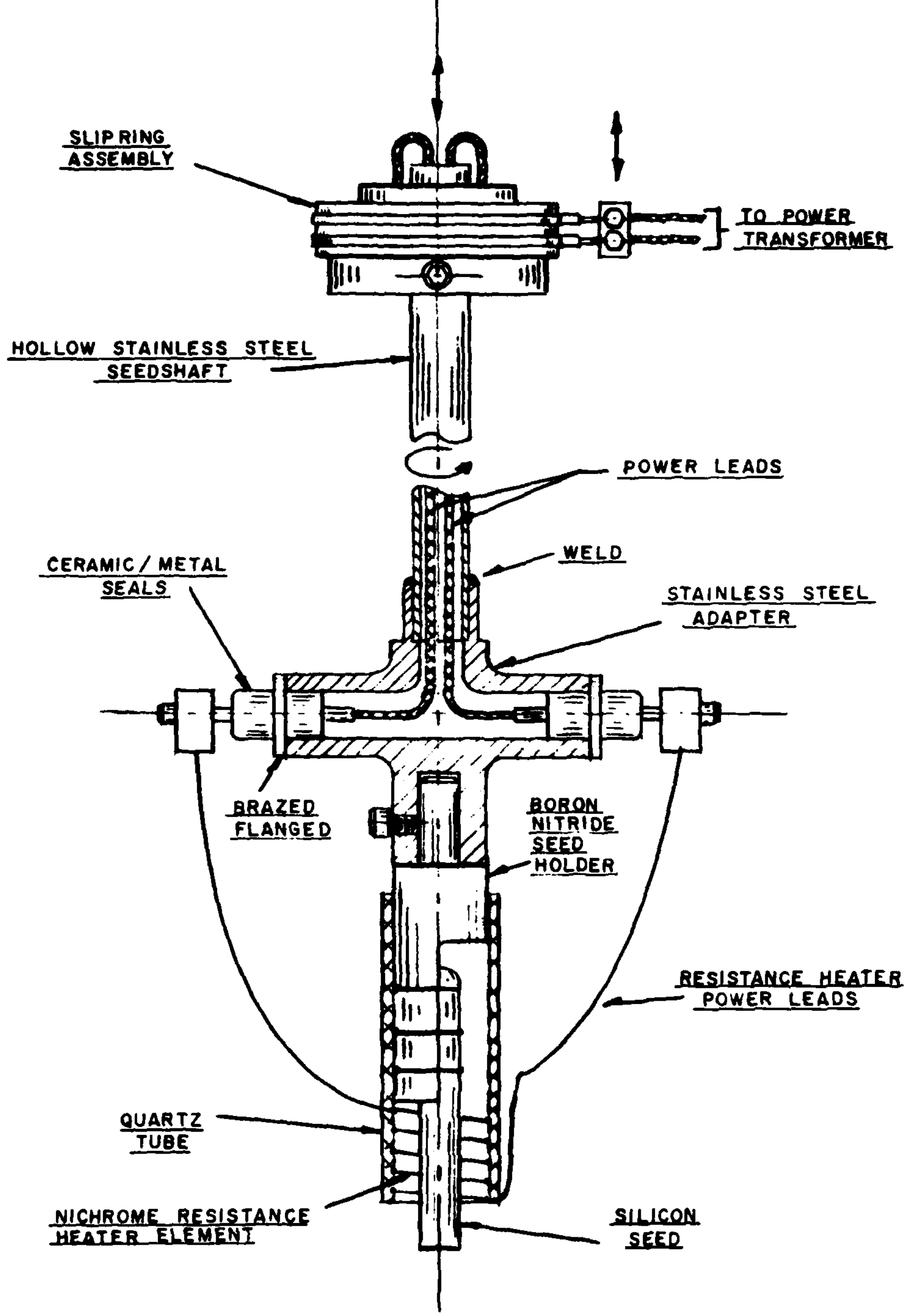


FIGURE 9 RESISTANCE HEATED SEED HOLDER

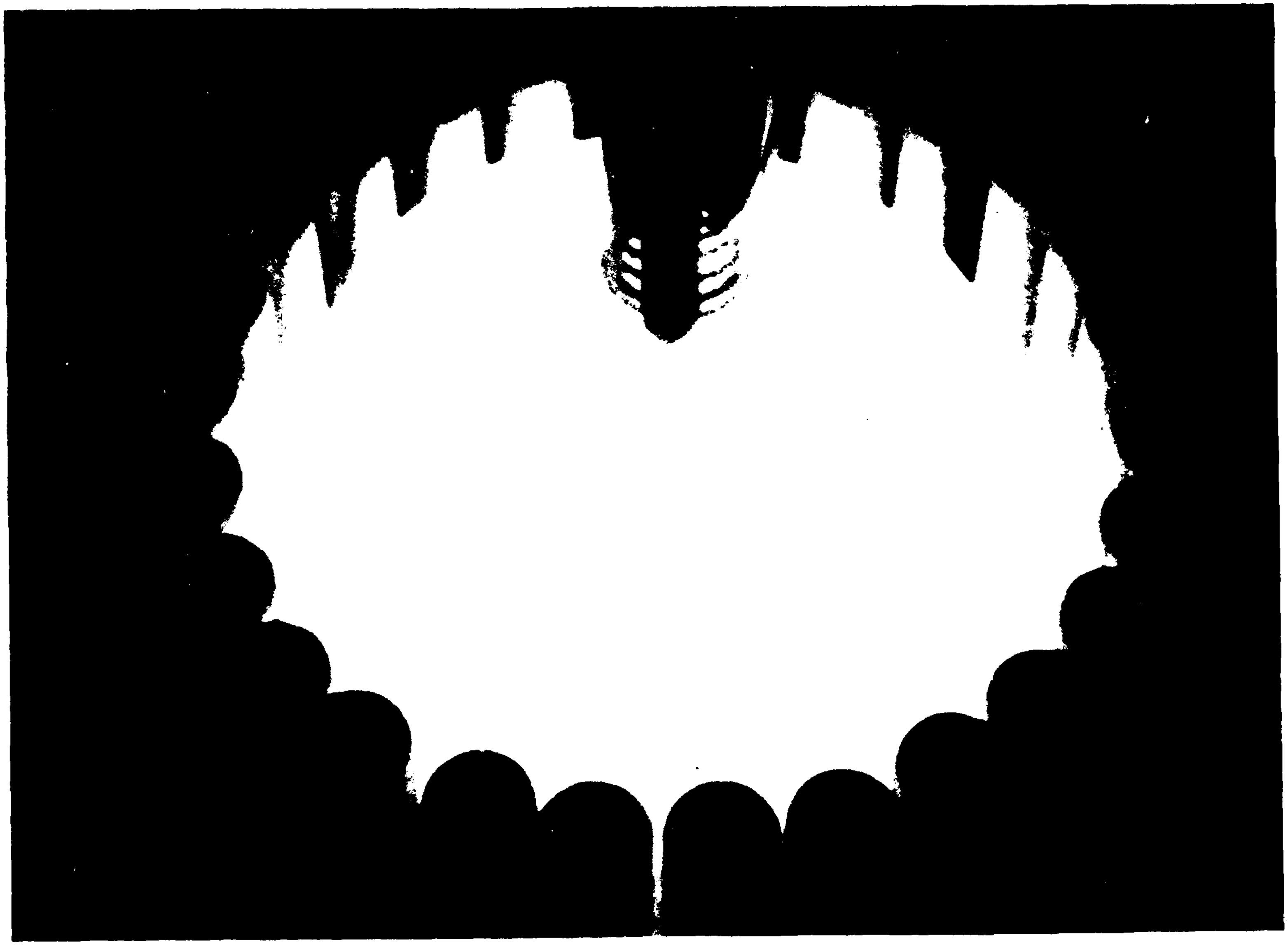


FIGURE 10 CRYSTAL PULLING EXPERIMENT UTILIZING THE RESISTANCE HEATED SEED HOLDER

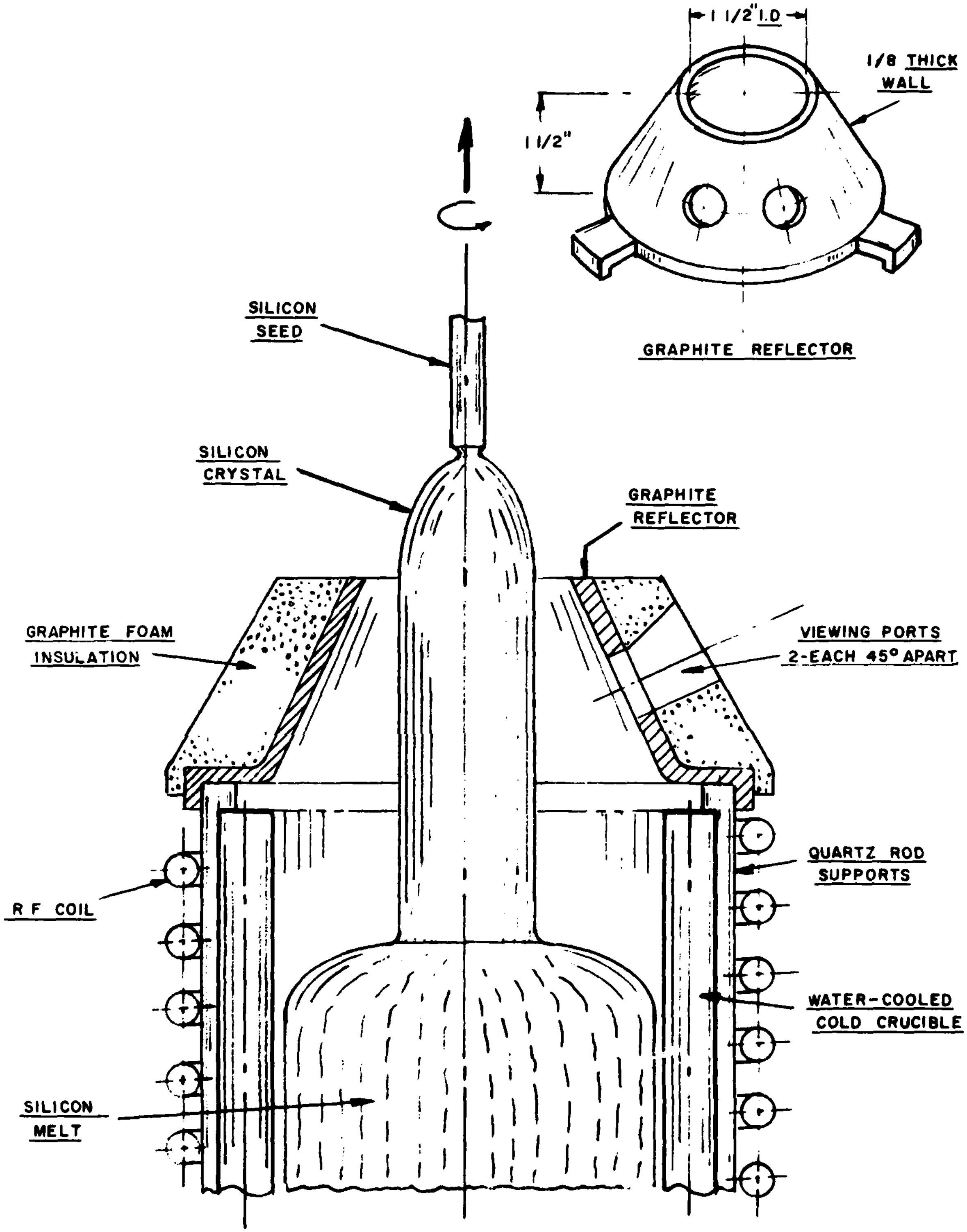


FIGURE 11

GRAPHITE REFLECTOR
USED FOR THE GROWTH OF SILICON CRYSTALS
FROM A MELT CONFINED IN A
COLD CRUCIBLE

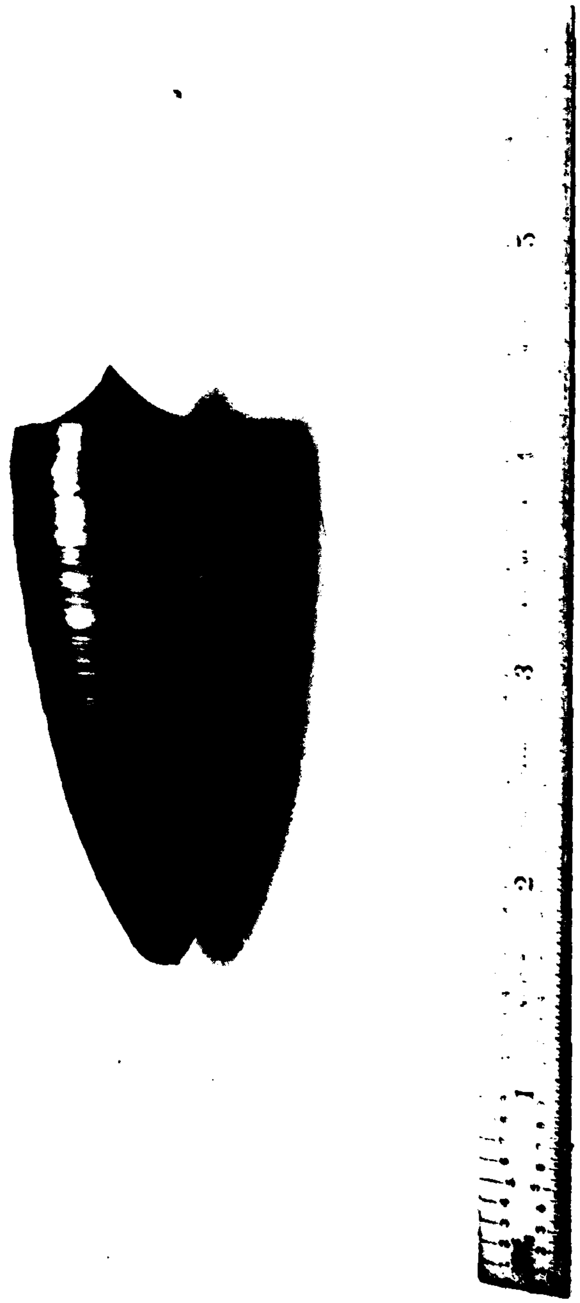


FIGURE 12 SINGLE CRYSTAL OF SILICON GROWN FROM A MELT CONFINED IN THE COLD CRUCIBLE

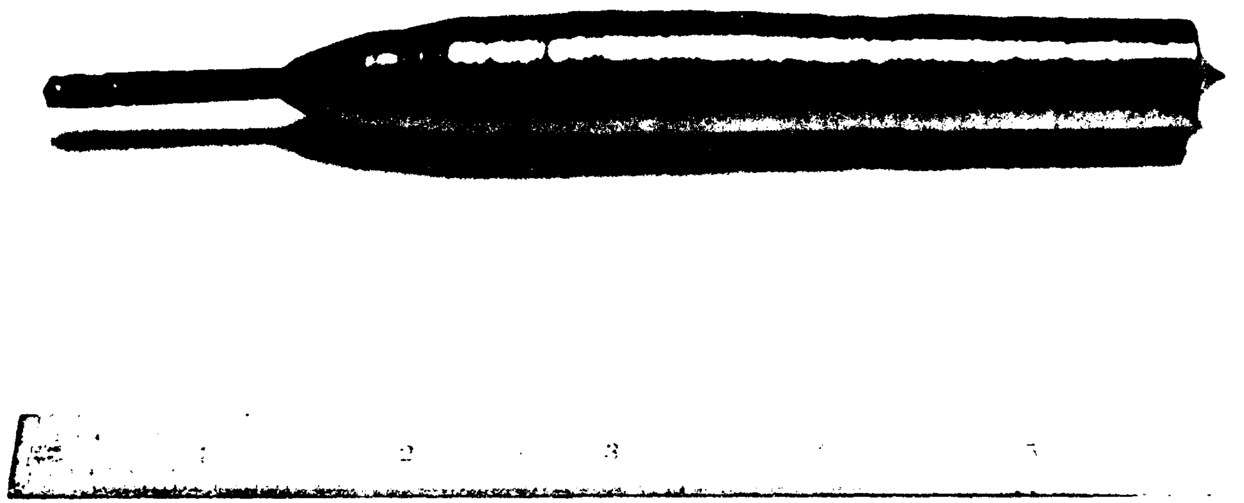


FIGURE 14 SINGLE CRYSTALS OF SILICON SHOWING THE CRYSTAL/MELT INTERFACE

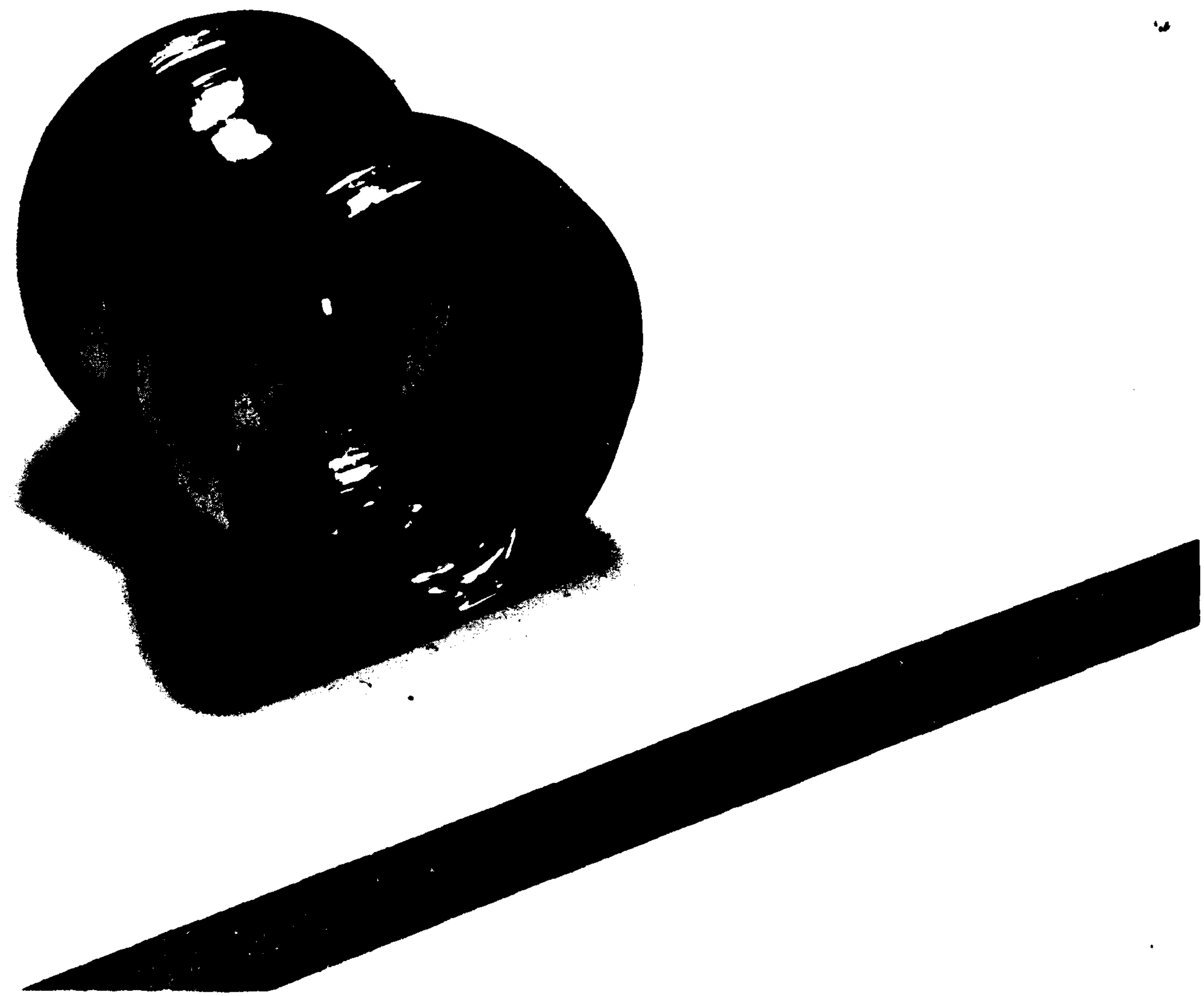
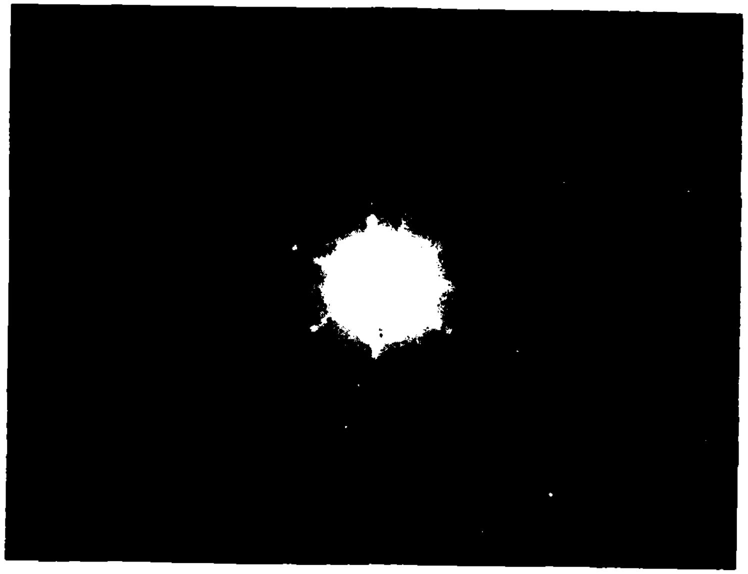
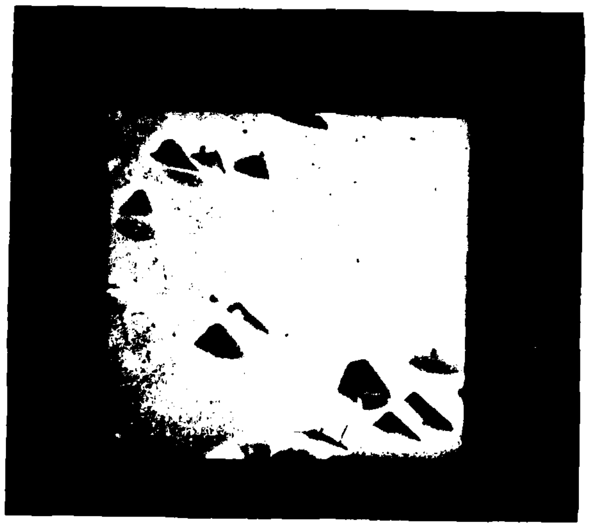


FIGURE 15 SINGLE CRYSTAL OF SILICON WITH HOLLOW-CORE CRYSTAL/MELT INTERFACE



Etched Surface Plane (111)

Etched Surface Plane



100 micron
x
100 micron
Area

$\boxed{10^{-4}\ cm^2}$

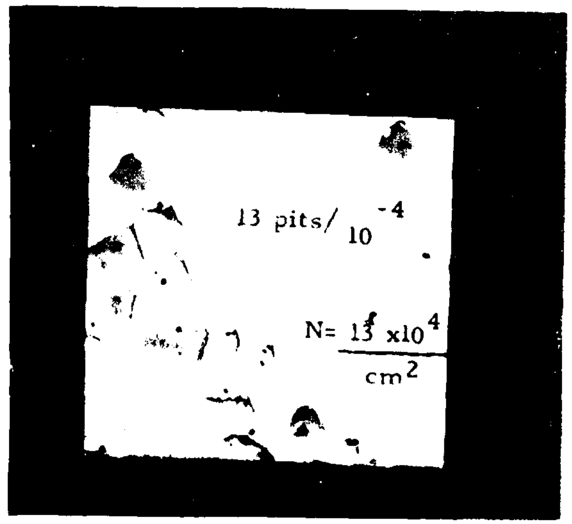
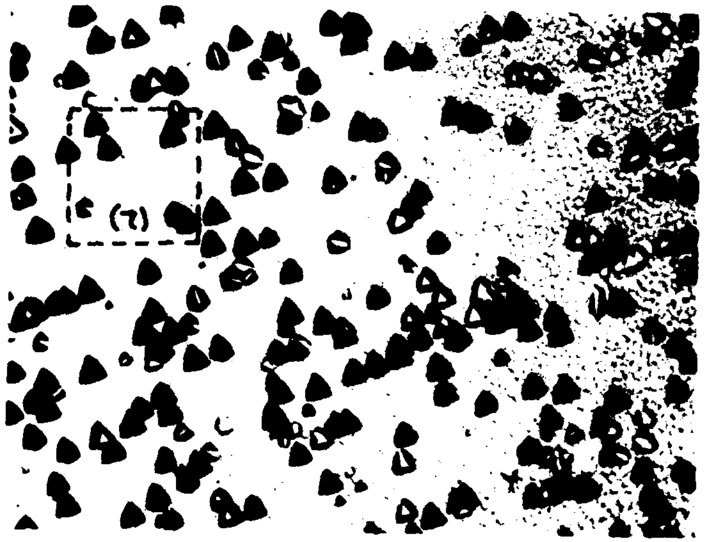


FIGURE 16 DISTRIBUTION OF DISLOCATIONS IN SINGLE CRYSTAL SILICON GROWN FROM A MELT CONFINED IN A COLD [illegible]

a) SEM Photograph

100 U = 100 micron = 10^{-2} cm :: Area = 10^{-4} cm^2



b) Optical Photograph 200 X

COLD CRUCIBLE SILICON

(Dislocation Density : Etch Pit Count on Surface)

Etch: 5 (70% HNO_3) : 3(48% HF) :3 (Glacial CH_3COOH)
followed by
Sirtl Decoration Etch ; 50 (100gr. CrO_3 /200 ml H_2O)
50 (48% HF)

Dislocation Density $\sim$ $(4\text{-}15) \times 10^4$ per cm^2

FIGURE 17 COLD CRUCIBLE SILICON/DISLOCATION DENSITY

3.0 CONCLUSIONS

A. The high electrical conductivity of molten silicon (10^4 mho/cm at 1420°C) effectively limits the maximum RF power which can be coupled directly to the melt confined in the cold crucible.

B. An external heat source is required to raise the temperature of the seed to insure wetting by molten silicon.

C. Use of the conical graphite reflector/radiator shield has permitted the reproducible growth of single crystals of silicon from melts confined in the cold crucible.

D. Preliminary analytical results show that the single crystals of silicon growth from melts confined in the cold crucible, have purity levels which are equal to, or in most cases, better than the semiconductor-grade poly-silicon feed material; this includes oxygen contamination.

E. Carbon content of the single crystals (approx. 2.6 PPM) is approximately twice that measured in the polysilicon feed material; we believe that the graphite radiator/reflector shield is the source of this impurity.

4.0 RECOMMENDATIONS

A. The preliminary analytical data on single crystals of silicon grown from melts confined in the cold crucible are inconclusive. At this point, it appears that the oxygen content of single crystals produced is about equal to that found in the polycrystalline silicon feed material but the absolute results obtained are subject to question. Further work on the characterization of these materials is certainly in order.

B. It appears that the graphite radiator/reflector shield may be the source of the carbon impurity found in the grown crystals. The graphite cone should be replaced with one fabricated from molybdenum or tantalum.

C. Little attention has been focussed on the growth of low dislocation silicon crystals from melts confined in the cold crucible. With resolution of the basic seeding technique, it will be neccessary to explore seed-necking/tapering methods in an attempt to reduce the dislocation density.

D. Experiments will be initiated to maintain a constant silicon melt level within the cold-crucible throughout the crystal pulling operation using the bottom-feeding arrangement which is already installed.

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